Validity of Various Approaches to Global Kinetic Modeling of Material Lifetimes

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Validity of Various Approaches to Global Kinetic Modeling of Material Lifetimes[1]

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Chemical kinetic modeling has been used for many years in process optimization, estimating real-time material performance, and lifetime prediction. Chemists have tended towards developing detailed mechanistic models, while engineers have tended towards global or lumped models. Many, if not most, applications use global models by necessity, since it is impractical or impossible to develop a rigorous mechanistic model. Model fitting acquired a bad connotation in the thermal analysis community after that community realized a decade after other disciplines that deriving kinetic parameters for an assumed model from a single heating rate produced unreliable and sometimes nonsensical results. In its place, advanced isoconversional methods, which have their roots in the Friedman and Ozawa-Flynn-Wall methods of the 1960s, have become increasingly popular. In fact, as pointed out by the ICTAC kinetics project in 2000, valid kinetic parameters can be derived by both isoconversional and model fitting methods as long as a diverse set of thermal histories are used to derive the kinetic parameters. The current paper extends the understanding from that project to give a better appreciation of the strengths and weaknesses of isoconversional and model-fitting approaches. Examples are given from a variety of data sets.

Isoconversional methods are undoubtedly the quickest way to derive kinetic parameters for complex reaction profiles involving multiple processes. However, isoconversional methods, sometimes called "model-free" kinetic analyses, are not assumption-free, and it is important to understand those assumptions and the limits they impose on predictions outside the range of calibration. The essential characteristic of the Friedman isoconversional method is that it is a sequential model. In practice, it is accomplished by establishing a form factor that transforms shape as a function of temperature or heating rate by having different activation energies associated with different extents of conversion. Alternatively, the form factor can be absorbed into an effective first-order frequency factor as long as the conversion step size is sufficiently small. Energetic materials appear to have reaction characteristics that are generally consistent with the isoconversional principle as long as the confinement conditions are constant and appropriate to the intended application.

Despite its strengths and common utility, the isoconversional principle is fundamentally inapplicable to reaction networks having competing reactions, in which the ultimate outcome of the reaction can be different depending on the temperature, and for concurrent reactions that change their relative reactivity over the temperature range of interest. Also, it is also not a good technique for sparse data sets or when the extent of conversion is incomplete and greatly different in different experiments, which is often the case with isothermal experiments.

Explicit models are potentially more flexible but suffer from issues of uniqueness. Explicit models can be either sequential or concurrent in nature, or any mixture thereof. Numerical integration techniques allow models of essentially any complexity to be used in an application mode, but unique calibration of many parameters by nonlinear regression becomes problematic without simplifying assumptions or independent experiments that emphasize or isolate different characteristics. If the reaction is fundamentally sequential in characteristic, a concurrent reaction model can have errors upon extrapolation outside the calibration interval.

A useful approach for heterogeneous materials is using parallel reactions with a distribution of activation energies and a common frequency, or occasionally, a frequency factor that increases exponentially with activation energy. An isoconversional model would work just as well in this situation as long as baseline correction issues can be overcome. On the other hand, an issue that arises in fossil fuel conversion, polymer decomposition, and energetic material decomposition is that competition between intermediate product escape and further reaction, either by itself or with unreacted material, causes a different set of products depending on temperature and confinement conditions. This situation is easily modeled, in principle, using traditional approaches, but it is not obvious how it can be modeled using the isoconversional approach.

> **Infinitely sequential model (Friedman isoconversional)**
> $-d(1-\alpha)/dt = f(\alpha)\,Ae^{-E/RT}$; $\ln(-d(1-\alpha))/dt) = -E/RT + \ln(Af(\alpha))$

> **Parallel "nucleation-growth" models (extended Prout-Tompkins)**
> $d\alpha/dt = \Sigma k_i(1-\alpha_i)^{ni}\,(1-q(1-\alpha_i))^{mi}$; $i=1$ to 3; A_i and E_i independent

> **Parallel nth-order models**
> $d\alpha/dt = \Sigma k_i(1-\alpha_i)^{ni}$; $i=1$ to 3; A_i and E_i independent

> **Discrete activation energy model**
> $d\alpha/dt = \Sigma k_i(1-\alpha_i)$; $i=1$ to 25; E_i evenly spaced; $\ln A = a + bE_i$
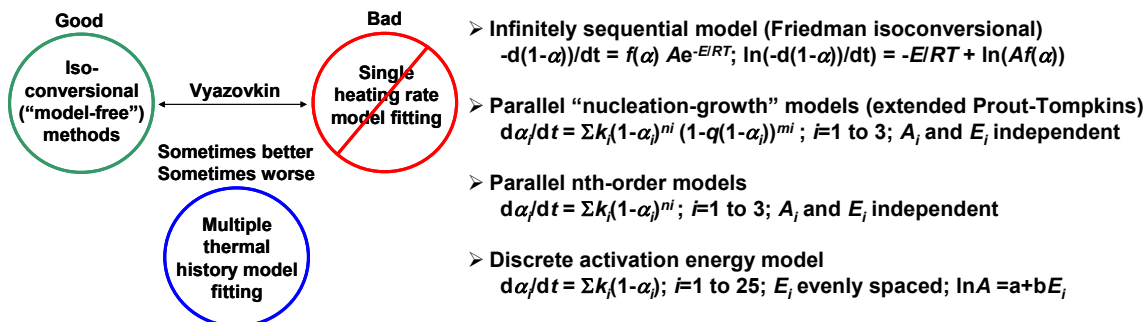
Fig. 1. The best way to derive kinetic models is of continuing interest. A variety of modeling approaches are considered here. All have limitations, and the best method depends on circumstances.

Ammonium Perchlorate Kinetic Parameters

Rxn 1	27% of total	Rxn 2	73% of total
A	1.36×10^7 s^{-1}	A	4.19×10^6 s^{-1}
E kcal/mol	22.8 kcal/mol	E	26.6
m	1.00	m	0.00
n	1.96	n	0.28

Fig 2. Model fitting works best when needs to mix endothermic and exothermic reactions in varying proportions in different circumstances.

Simulated data: ICTAC 2006

The heating rates of 0.25, 1.0, 2.0, 4.0, and 8.0 °C/min

Isoconversional

Discrete E distribution

Parallel nth-order

Predicted % reacted for three years at the specified temperatures

Model	25 °C	50 °C	80 °C	25±10	50±30
Isoconversional	3.11	24.97	72.62	5.19	54.43
Discrete E distribution	4.51	24.80	70.43	6.49	52.95
3-parallel nth-order	3.27	25.47	69.56	5.67	54.50
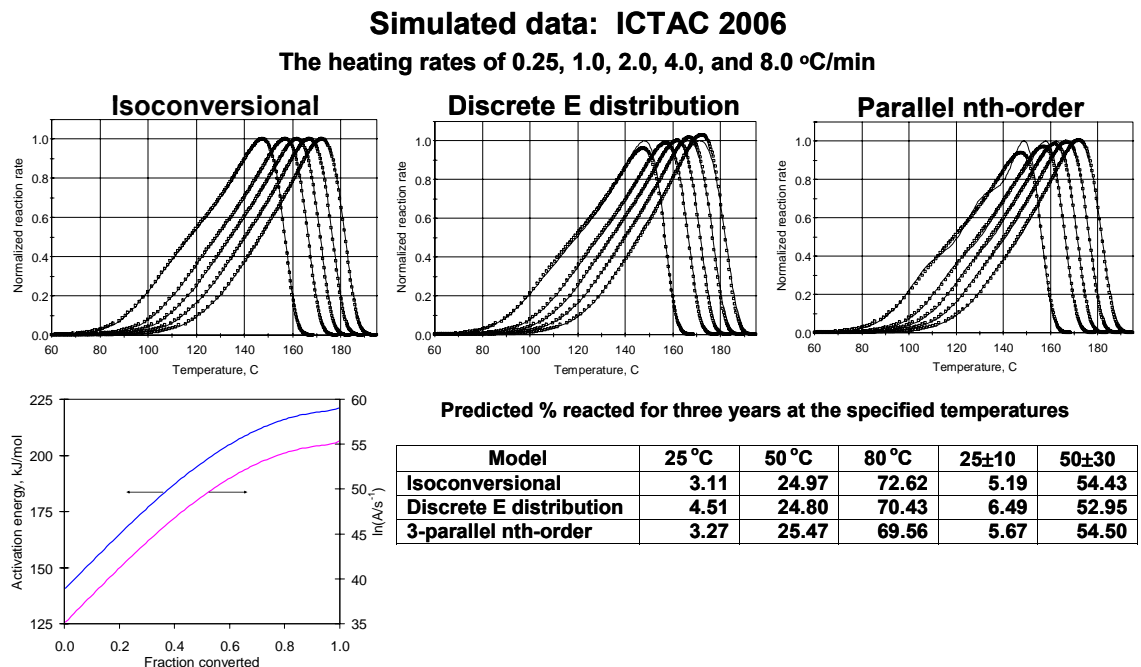
Fig. 3. For systems with a monotonically increasing activation energy, isoconversional and parallel reaction models work equally well.

Isoconversional model

0.5-3.0 °C/min

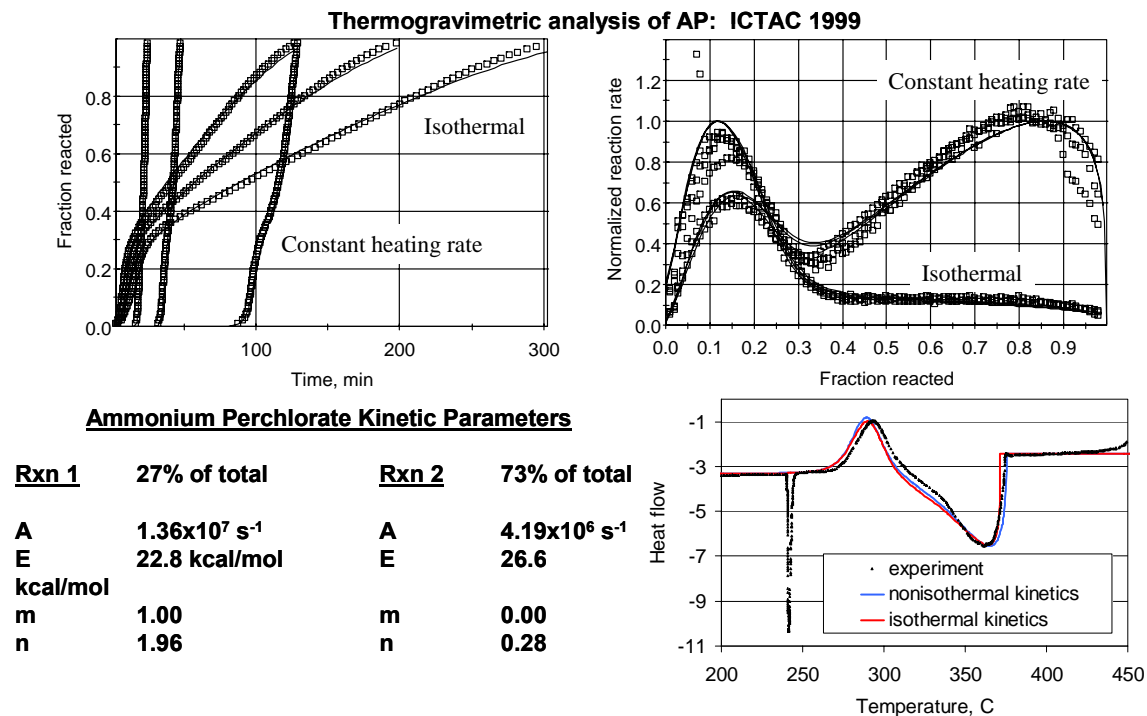### Parallel nucleation-growth model

0.5-3.0 °C/min

E LLNL1
E LLNL2
E AKTS
ln(A) LLNL1
ln(A) LLNL2
ln(A) AKTS

ICTAC propellant sample 4

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.238	3.79×10^{9}	103.63	0.82	0.76
0.493	2.43×10^{15}	153.31	0.96	1.06
0.269	6.41×10^{15}	110.49	0.93	1.38

Fig 4. For multi-step decomposition of energetic materials, sometimes the activation energy decreases with conversion. The important point for lifetime prediction is whether the underlying reaction network is parallel or sequential in nature.

Sample B3

Legend:
- LLNL lin isoconv
- LLNL nl isoconv
- LLNL nl 3 nuc-gr
- AKTS isoconv1
- AKTS isoconv2

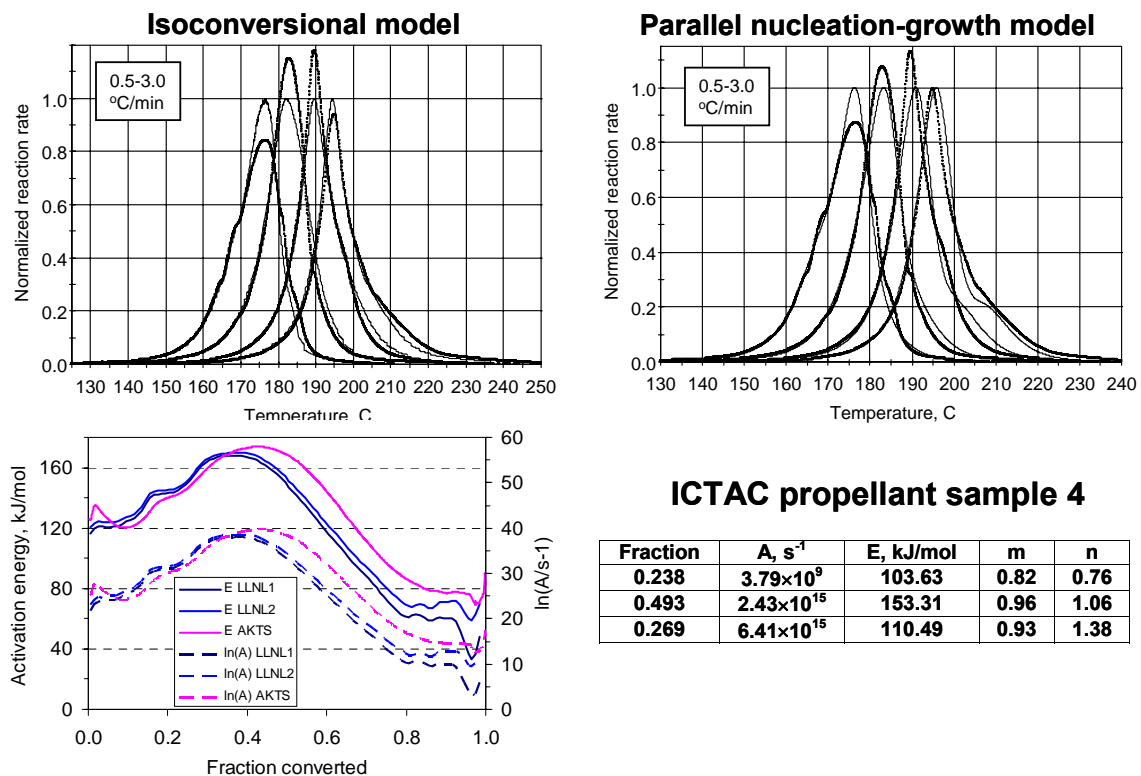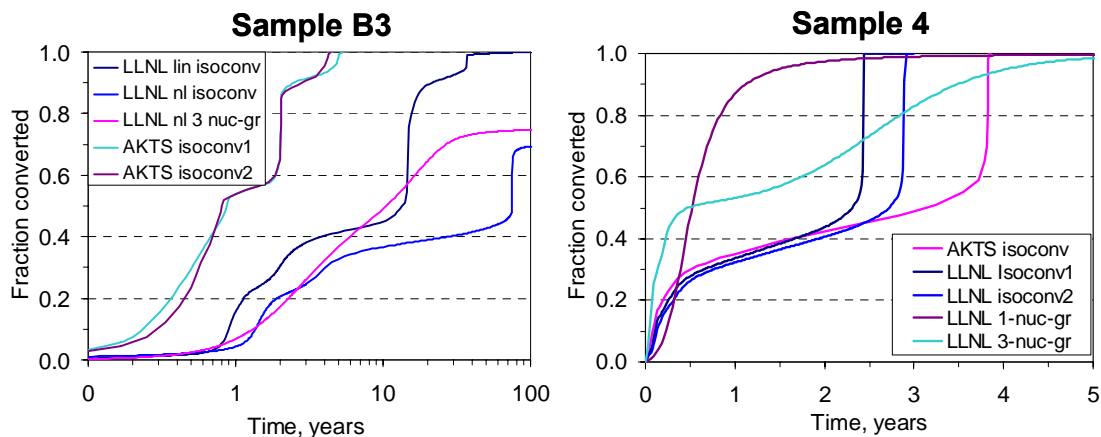Fraction converted vs Time, years

Sample 4

Legend:
- AKTS isoconv
- LLNL Isoconv1
- LLNL isoconv2
- LLNL 1-nuc-gr
- LLNL 3-nuc-gr

Fraction converted vs Time, years

Fig. 5. Differential isoconversional models can successfully mimic the delayed autocatalysis often seen in propellant aging, while parallel nucleation-growth models tend to have aging processes switch order. However differential isoconversional models are very sensitive to baseline selection when the baseline is not smooth.
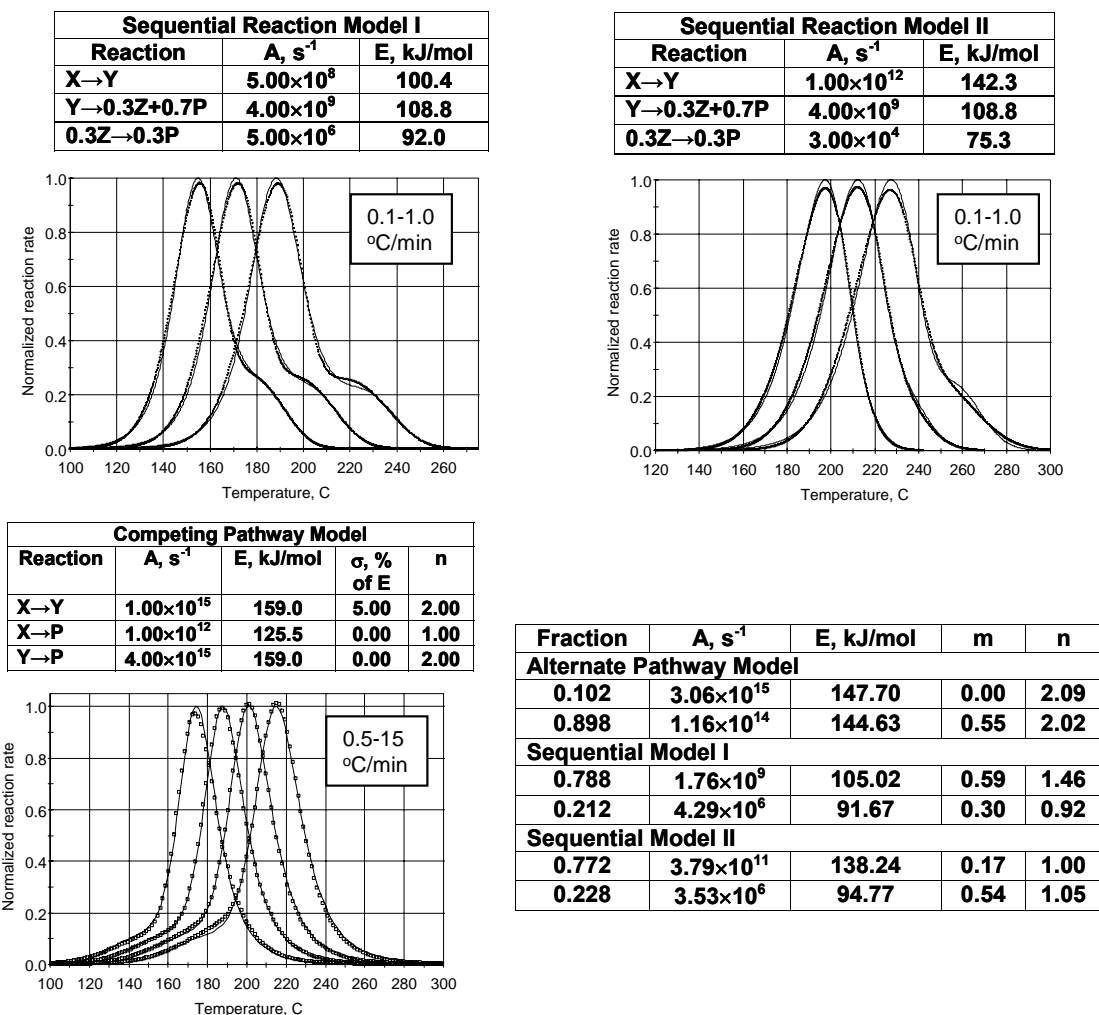
Sequential Reaction Model I		
Reaction	A, s^{-1}	E, kJ/mol
X→Y	5.00×10^{8}	100.4
Y→0.3Z+0.7P	4.00×10^{9}	108.8
0.3Z→0.3P	5.00×10^{6}	92.0

Sequential Reaction Model II		
Reaction	A, s^{-1}	E, kJ/mol
X→Y	1.00×10^{12}	142.3
Y→0.3Z+0.7P	4.00×10^{9}	108.8
0.3Z→0.3P	3.00×10^{4}	75.3

0.1-1.0 °C/min

0.1-1.0 °C/min

Competing Pathway Model				
Reaction	A, s^{-1}	E, kJ/mol	σ, % of E	n
X→Y	1.00×10^{15}	159.0	5.00	2.00
X→P	1.00×10^{12}	125.5	0.00	1.00
Y→P	4.00×10^{15}	159.0	0.00	2.00

0.5-15 °C/min

Fraction	A, s^{-1}	E, kJ/mol	m	n
Alternate Pathway Model				
0.102	3.06×10^{15}	147.70	0.00	2.09
0.898	1.16×10^{14}	144.63	0.55	2.02
Sequential Model I				
0.788	1.76×10^{9}	105.02	0.59	1.46
0.212	4.29×10^{6}	91.67	0.30	0.92
Sequential Model II				
0.772	3.79×10^{11}	138.24	0.17	1.00
0.228	3.53×10^{6}	94.77	0.54	1.05

Fig. 6. Three additional simulated data sets were created and analyzed by both parallel nucleation-growth and isoconversional kinetic models.

Competing pathway model

Sequential reaction model I

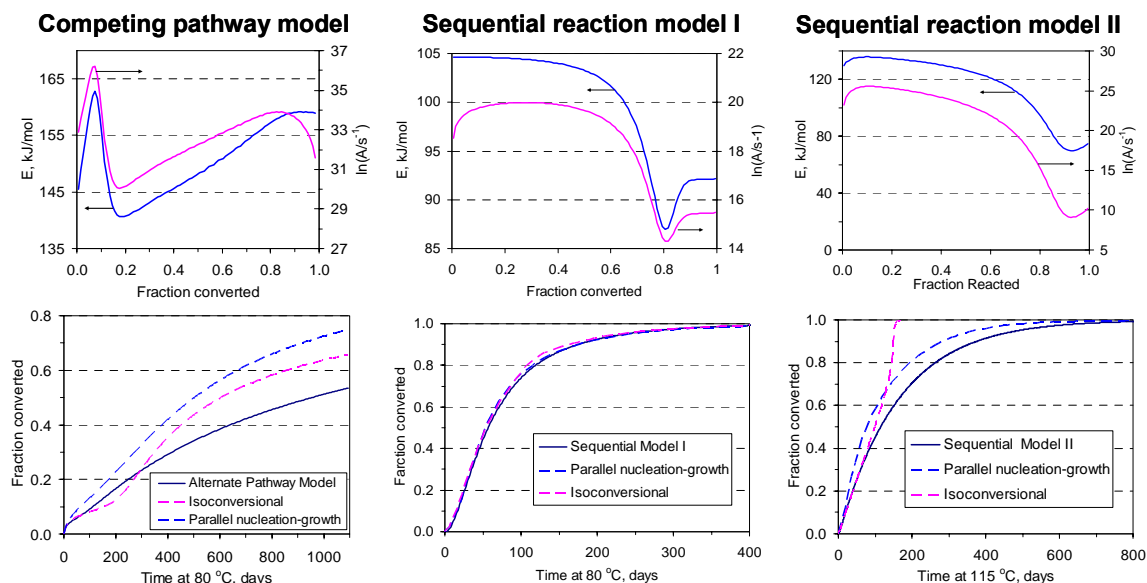**Sequential reaction model II**

Fig. 7. Differential isoconversional and model fitting approaches have comparable reliability—sometimes one works better and sometimes the other. A good fit to data does not guarantee accurate extrapolation. Self-consistency between the two approaches substantially increases confidence for extrapolation.
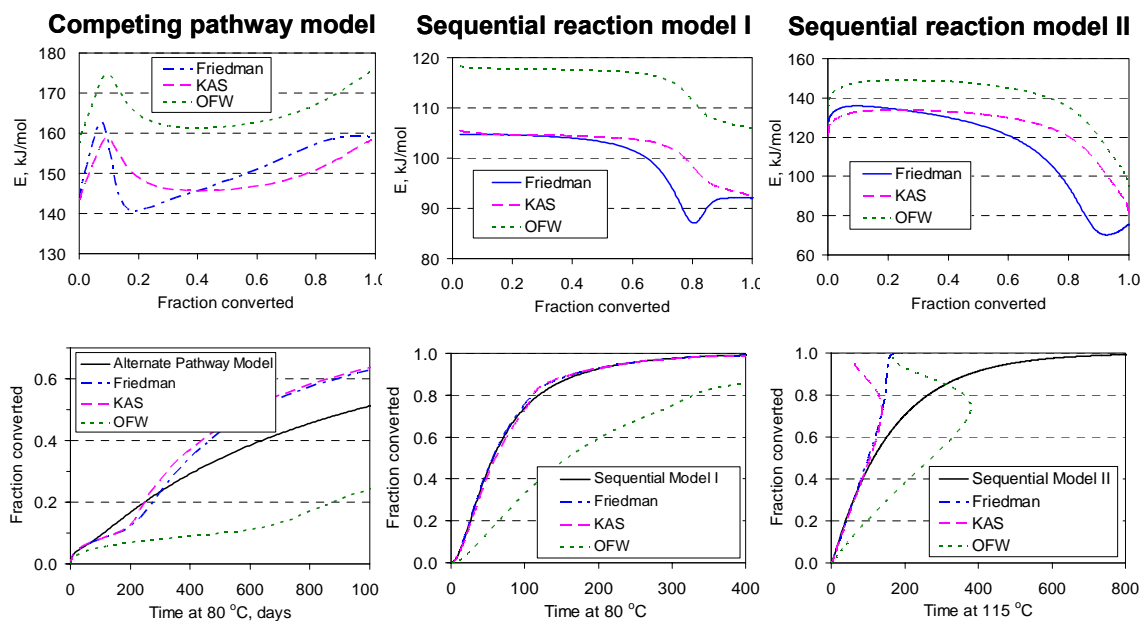
Competing pathway model

Sequential reaction model I

Sequential reaction model II

Fig. 8. Some integral isoconversional kinetic methods are not as reliable. The popular Ozawa-Flynn-Wall method significantly overestimates activation energies and gives poor extrapolations. The traditional way of predicting conversion for integral isoconversional methods fails when the activation energy drops substantially as a function of conversion. Piecewise integral isoconversional methods solve that problem but have no intrinsic advantage over differential isoconversional methods.